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Density-functional calculations of the elastic properties of some polymer chains

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The force constants and elastic properties of some polymers are calculated with a full-electron, crystal-orbital density functional method. Calculations are carried out on single helical chains of polyethylene, polytetrafluoroethylene (teflon), polyglycine (nylon-2), and nylon-3. The longitudinal elastic moduli are obtained both from the Hessian and by direct elongation relaxations. The different degrees of freedom of the polymers are ranked according to their contributions to the elastic response. It is shown, that a proper choice of the internal coordinates makes it possible to keep some of them frozen during the process without a considerable loss of elasticity.

I. INTRODUCTION

The calculation of the elastic properties of polymer chains from theory has been carried out by several authors using from semiempirical to first principles methods. However the basic scheme is similar in all of these models. First the equilibrium structure is determined and after that, the elastic properties are determined from the properties of the energy hypersurface at this point. The main difference among these models is the method that provides the required potential energy surface. The first family of these models is based on molecular force fields that substitutes the quantum mechanical interaction of particles in the molecule with classical interactions and uses classical mechanical laws to determine the potential energy surface. In the second family of the models, the potential energy surface is calculated quantum mechanically either using solid state physical approaches or quantum chemical methods. In the solid state approach the polymer chains are ordered in a three-dimensional crystal structure and the distance of the neighboring chains are chosen large enough to neglect the interchain interaction. In the quantum chemical approaches the chain properties can be derived from oligomer calculations. These methods use only a finite part of the polymer to calculate the elastic properties and try to reach the convergence by increasing the length of the finite chain. This method suffers from the ‘‘end effect,’’ the structure of the finite chain differs from the structure of the infinite polymer. One of the possible solutions of this problem is the cluster difference method used by Crist and Hereña[1] that minimizes the influence of the chain ends on the repeat unit energy by substracting the total energy of oligomers containing $M+1$ and M repeat units.

This problem does not arise if the helical symmetry of the infinite polymer chain is used explicitly in the chain direction as it was used by several authors.[2–9] In our approach the potential energy surface of a single infinite chain is treated by first principles density functional method (DFT), the helical symmetry along the polymer chain axis is utilized.

The outline of our paper is as follows. In Sec. II we summarize the theory of the calculation of the elastic properties of quasi one-dimensional polymer chains. The main features of the DFT polymer program used and the details of the numerical realization are also given in this paragraph. The calculated elastic properties of two vinyl type polymers (polyethylene PE and polytetra fluoroethylene) and two polyamides (polyglycine and nylon-3) are described in Sec. III.

II. METHOD

A. Treatment of helical chains with DFT

The total energy calculations are carried out with the POLYXA program[10] of Mintmire. Details about the code are published elsewhere; here the main features which are important for the present results are summarized. Full-electron single point total energy calculations are done with crystal orbitals. The crystal orbitals[11–13] are expanded in Bloch orbitals built from Gaussian atomic basis sets. The infinite helical chain is subjected to a density functional (DFT) self-consistent field calculation. The Slater-Gáspár-Kohn-Sham local density exchange is combined with the Perdew-Zunger parametrized[14] correlation potential based on the Ceperley-Alder data.[15] Periodic boundary conditions are used but no finite neighbor approximation has been done. A triple va-

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lence zeta basis set with polarization functions (TZVP) of Godbout *et al.*[16] is used throughout the calculations.

B. Force constants and longitudinal elastic properties

The total energy of a general infinite polymer chain with helical symmetry is considered as a function of the nuclear frame geometry. In the Born-Oppenheimer approximation the nuclear frame is held fixed while the corresponding electronic state is obtained. In the general case (with no special symmetries) N number of nuclei in the repeat unit of the helix (unit cell) have $3N-6$ internal nuclear coordinates, the position and the orientation of the screw axis with the two parameters fixing the screw operation gives six degrees of freedom, which in total results in $3N$ degrees of freedom for the whole helical chain. Choosing appropriate parameters $(x_1,x_2,\ldots,x_n)=\mathbf{x}$ with $n\leqslant 3N$ the conformation of the polymer is given and a single valued $E(\mathbf{x})$ energy can be calculated. A fixed nuclear conformation determines the linear size of the system via a *geometrical* relation $c=c(\mathbf{x})$. This typical linear extension for an infinite helix is chosen to be the translational distance in the screw operation. The response of the system with respect to elongations along the chain axis is characterized by the total energy at a given length defined as

$$E(c)\doteq\min_{\mathbf{x}\in\Gamma_c}E(\mathbf{x})=E[\mathbf{x}(c)],\tag{1}$$

where Γ_c is the set of those configurations which results in a given c. This minimization provides a way in which the $c=c(\mathbf{x})$ geometrical relation can be in a certain sense ''inverted'' to $\mathbf{x}=\mathbf{x}(c)$.

Around the equilibrium configuration of the system $(\mathbf{x}_0,c_0,E_0,\ldots)$ the harmonic response to small elongations is given by the force constant

$$\mathcal{F}\doteq\left.\frac{d^2}{dc^2}E(c)\right|_0 .\tag{2}$$

For single chain infinite polymers the more relevant quantity is the longitudinal elasticity counted per unit length with the definition

$$f\doteq c_0\mathcal{F}.\tag{3}$$

Whenever a cross section area A can be attributed to the chain (e.g., for crystallinelike parallel chains) the Young's modulus is related to these constants as

$$Y\doteq\mathcal{F}\frac{c_0}{A}=\frac{f}{A}.\tag{4}$$

In the direct ''elongation-relaxation'' methods one calculates the response of the system to elongations by deforming the equilibrium geometry so that the length changes. Keeping this nonequilibrium length unchanged a constrained reoptimization of the structure is required. Calculations for several strains samples $E(c)$ with a small number of points $\{E(c_i)\}_i$ from which the second derivative around the minimum can be calculated by fitting the data. This method has been extensively used[2–6] for single chains and for the solid state of polymers.

The Young's modulus is however an equilibrium property of the system. The connection of it with the other equilibrium quantities

$$\mathbf{g}_i\doteq\left.\frac{\partial c(\mathbf{x})}{\partial\mathbf{x}_i}\right|_0,\quad \hat{\mathbf{F}}_{i,j}\doteq\left.\frac{\partial^2E(\mathbf{x})}{\partial\mathbf{x}_i\partial\mathbf{x}_j}\right|_0\tag{5}$$

is given by the exact relation

$$\mathcal{F}=(\mathbf{g},\hat{\mathbf{F}}^{-1}\mathbf{g})^{-1}\tag{6}$$

as it is derived in the Appendix. This expression is directly applicable whenever the (invertible) Hessian $\hat{\mathbf{F}}$ of the system is given. Hong and Kertész[7] used a scheme equivalent to the above one in order to calculate the Young's modulus from semiempirical and ''spectroscopical'' force constants.

The full Hessian contains a lot more information than what is needed for the longitudinal elastic response. The evaluation of all the second partial derivatives might be too expensive or even practically unrealizable for a complex system, for which the Young's modulus could have been calculated in an easier way by, e.g., the direct method. In this paper we investigate which coordinates are important in order to obtain a good approximate characterization of the elastic properties from a reduced set of degrees of freedom. The use of the full Hessian is a powerful tool to carry out such a study. The Hessian calculated in one coordinate set $\mathbf{x}=(x_1,x_2,\ldots,x_n)$ is easily transformed to another $\mathbf{y}=(y_1,y_2,\ldots,y_m)$, possibly reduced $(m\leqslant n)$ one with the aid of the Jacobian matrix $\hat{\mathbf{J}}=\partial\mathbf{y}/\partial\mathbf{x}$ as

$$\hat{\mathbf{F}}_{\mathbf{y}}=\hat{\mathbf{J}}^{\mathbf{T}}\hat{\mathbf{F}}_{\mathbf{x}}\hat{\mathbf{J}}.\tag{7}$$

In particular in a *reduced set* of coordinates, where the reduction is done with constraints which are automatically satisfied at the equilibrium configuration (e.g., fixing a coordinate to its equilibrium value) one has

$$\mathcal{F}_{\mathbf{y}}=(\dot{\mathbf{y}},\hat{\mathbf{F}}\dot{\mathbf{y}})\geqslant\mathcal{F}_{\mathbf{x}}\tag{8}$$

because of the variational nature of Eq. (1) with respect to the enlargement of the configuration space. The relative difference

$$\Delta\mathcal{F}=\frac{\mathcal{F}_{\mathbf{y}}-\mathcal{F}_{\mathbf{x}}}{\mathcal{F}_{\mathbf{x}}}\tag{9}$$

measures the contribution of the omitted degrees of freedom to the longitudinal elastic modulus.

C. Numerical realizations

1. Structural optimization

Although for the polymers treated here one can find the structure both from experiments and from papers on structural optimization, one has to carry out an optimization when the second derivatives of the energy are in question. The system must be in the harmonic regime with respect to small changes in the parameters around their relaxed values; the Hessian of the system should be positive definite. In our case it was achieved with adjusting the configuration until the maximal component of the energy gradient became smaller than a given tolerance typically around 10^{-3}–10^{-4} (understood in hartree/Å or hartree/radian). The numerical gradients are calculated from single point total energy calculations with finite differences upon changing the parameters in the order of magnitude 10^{-4}–10^{-5} (Å or radian). We have tried several optimization algorithms, the most reliable and economic we found and used was the Broyden-Fletcher-Goldfarb-Shanno one.[17] Starting from a reasonable guess on the equilibrium coordinates the relaxation was found in about the same number of steps as the number of optimization parameters.

2. Elongation relaxation

Our method consisted of the following steps.

(1) First we make a full optimization of the unconstrained energy. In addition to evaluating the energy gradients in each relaxation step we also evaluate the gradient **g** of the length as a function of the internal configuration parameters. These derivatives are calculated numerically. Although there might be a way to use the analytical geometrical relation $c(\mathbf{x})$ to get these gradients, this relation could be too complicated for nonsimple unit cells. Regarding the overall loss of precision in the full calculation, there is no need to have the exact gradients instead of the numerical ones.

(II) Next, we elongate the chain. In a complex polymer the cell length itself is rarely chosen as an independent optimization parameter. The screw parameters are often more conveniently defined with the use of internal coordinates between nuclei in neighboring unit cells. Without a direct control of the cell length there is an ambiguity as to how to change the internal parameters to achieve a desired chain elongation. It is reasonable to select deformations proportional to **g**. If a strain

$$\varepsilon=\frac{\Delta c}{c}\cong\frac{(\mathbf{g},\mathbf{\Delta x})}{c} \tag{10}$$

is required, the following choice of parameter changes is appropriate:

$$\mathbf{\Delta x}=\frac{c\varepsilon}{(\mathbf{g},\mathbf{g})}\mathbf{g}. \tag{11}$$

(III) Then we carry out a constrained optimization of this deformed configuration. The constraint can be taken into account as in Eq. (A1), i.e., at each relaxation step the component of the energy gradient normal to the constraint surface (parallel to **g**) is to be canceled before making a step.

(IV) Typically we use five points with strains: $(0, \pm 0.77\%, \pm 1.23\%)$. These small distortions make it possible to relax the strained system with 3–4 relaxation steps to the desired accuracy. This is rather important in the case of a complex polymer, where one has a large number of parameters for which the calculation of the full Hessian is practically impossible.

3. Second derivatives and inverse Hessian

The Hessian is calculated with finite difference method; three-point formulas are used for the diagonal elements, seven-point for the mixed partial derivatives. All points in the configuration space are symmetric with respect to the central point (assumed minimum). We use displacements typically in the range of 10^{-3}–10^{-2} (in Å or radian). Higher precision is unreliable because of the numerical noise, lower is inappropriate in order to stay in the harmonic region. A careful optimization followed by a numerical differentiation in this way gives numerical second derivatives with precision not worse than ± 0.03. This has been tested by varying the threshold for optimization, choosing different coordinates to describe the polymer, using different step size, etc. The final Young's modulus is compared with the elongation-relaxation one and shows, that the corresponding force constants are good within the precision given.

The polymers treated here have symmetries that make it possible to reduce the maximal $3N$ number of independent degrees of freedom. The Young's modulus can already be calculated from the minimum number of such parameters, assuming, that the symmetry is preserved or the breaking of it has a negligible contribution to the longitudinal force constant.

The Hessian matrix elements obtained here refer to the ''in phase'' or $k=0$ lattice vibrations, i.e., the deformations in the unit cell are repeated periodically in all cells. This makes it difficult to compare the Hessian with that of a molecule if the intercell coupling is not negligible. For example, we have one r_{CC} per unit cell for polyethylene, but when changing it we change this length over the whole chain. The cumulative force constant is

$$F=F^{[0]}+2\sum_{n=1}^{\infty}F^{[n]}, \tag{12}$$

where $F^{[0]}$ is the ordinary diagonal force constant for elongating exactly one r_{CC} bond in the polymer as supermolecule, whereas $F^{[n]}$ is an off-diagonal constant describing the coupling of two bond elongations done in two different cells that are nth neighbor to each other.

The inversion of the Hessian is needed in order to use Eq. (6) to obtain the longitudinal force constant. Care should be taken with nondefinite or poorly definite Hessians. Negative eigenvalues can appear because of imprecise optimization, whereas zero or small eigenvalues can enter if such degrees of freedom are also considered, which do not have strong influence on the energy. The elimination of these coordinates is done by diagonalizing the Hessian

$$\hat{\mathbf{U}}^{\dagger}\hat{\mathbf{F}}\hat{\mathbf{U}}=\hat{\mathbf{\Omega}},\quad \hat{\mathbf{\Omega}}_{i,j}=\omega_i\delta_{i,j} \tag{13}$$

and using

$$(\mathbf{g},\hat{\mathbf{F}}^{-1}g)^{-1}\approx\left(\sum_{\omega_i>+\epsilon}\frac{h_i^2}{\omega_i}\right)^{-1},\ \mathbf{h}=\hat{\mathbf{U}}^{\dagger}\mathbf{g}. \tag{14}$$

Omitting small eigenvalues is allowed only if the corresponding h_i^2 are small, in which case the indefinite 0/0 limit is being excluded.

III. RESULTS

A. Vinyl polymers

For both polyethylene (PE) and polytetrafluoroethylene (PTFE) the (nontranslational) unit cell consists of one [-CX_2-] group, where X is understood to be H for PE and F for PTFE. The helix is built with a screw operation involving

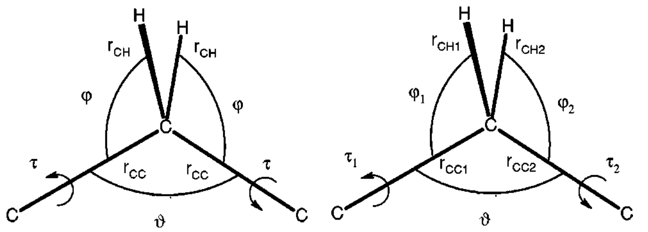

FIG. 1. Internal coordinates of polyethylene utilizing the full symmetry (left panel) and without symmetry restrictions (right panel).

a rotation of the cell with 180° combined with a translation, the distance of which is referred to as the cell length (c). The assumed symmetry makes it possible to use the minimal number of four free parameters fixing a configuration of the chain. However this minimal set of parameters gives rise to misleading effects, that is to be seen in the example of polyethylene. For a better understanding of the elastic response the release of symmetry requirement and the use of more configurational parameters turns out to be more appropriate.

1. Polyethylene

The planar zigzag conformation is known to be the equilibrium structure. The minimal set of parameters to build the full-symmetric chain were chosen as: CC bond distance (r_{CC}), CCC bond angle (ϑ), CH length (r_{CH}), and CCH bond angle (φ), as shown in the left panel of Fig. 1. The optimized values of the parameters obtained with our treatment are listed in Table I. They compare well with other published data.[18,20–22] The column $\Delta\mathcal{F}$ measures the importance of the different degrees of freedom in the elastic process. These numbers show the increase of the longitudinal force constant if the corresponding variable is kept fixed at its equilibrium value. For example, $\Delta\mathcal{F}=16.3\%$ for variable φ gives the relative error in the Young's modulus [according to Eq. (9)] if it were calculated using the reduced $\mathbf{y}=(r_{\mathrm{CC}},r_{\mathrm{CH}},\vartheta)$ coordinate set instead of the full $\mathbf{x}=(r_{\mathrm{CC}},r_{\mathrm{CH}},\vartheta,\varphi)$ one. From Table I one concludes, that the two most important elastic degrees of freedom are the CC bond stretching and the bending of the CCC bond angle. The change in CH bond length does not contribute to the Young's modulus, it can be kept frozen at its equilibrium value, as is intuitively expected. The noticeable role of the CCH bond angle φ is surprising. Hong and Kertész[7] also observed this phenomenon, namely, that the CCH bond angle is strongly coupled to the CCC bond angle and the relaxation of it significantly reduces the modulus of the polymer. The coupling constant in the present calculations is found to be $F_{\vartheta\varphi}=0.61$ which is large compared to the diagonal element $F_{\vartheta\vartheta}=0.46$ and consequently reduces the rigidity of changing the CCC bond angle. This is but a misleading artifactual effect of using this minimal set of coordinates. When one specifies the CH bonds with their two bond angles to the neighboring CC bonds, the deformation of the CCC angles changes the orientation of the CH bonds heavily. The $F_{\vartheta\vartheta}$ force constant includes this effect of changing the CH bond alignment to a great extent. This must be compensated with a subsequent relaxation of the CCH bonds not to distort the tetrahedral group so much. We have carried out independent calculations treating all the nine degrees of freedom of PE without symmetry constraints. The standard coordinates used are r_{CC}, CC bond distance; $r_{\mathrm{CH}i}$, CH_i bond distances; ϑ, CCC bond angle; φ_i, CCH_i bond angles; τ_i, CCCH_i improper torsion angles; and CCCC dihedral angles (right panel of Fig. 1). This last angle is not listed in Table II, as its small distortions from the 180° value of the planar configuration has too small of an effect on the energetics of the system. Although symmetry has not been forced, the optimized geometry is found to be symmetric. The spontaneous conservation of the symmetry makes it possible to consider the transformation $(r_{\mathrm{CC}},r_{\mathrm{CH1}},r_{\mathrm{CH2}},\vartheta,\varphi_1,\varphi_2,\tau_1,\tau_2)\rightarrow(r_{\mathrm{CC}},r_{\mathrm{CH}},\vartheta,\varphi)$ between the two parametrizations of Fig. 1. Using the Jacobian matrix of $r_{\mathrm{CH}}=r_{\mathrm{CH1}}=r_{\mathrm{CH2}}$, $\varphi=\varphi_1=\varphi_2$, $\tau=\tau_1=-\tau_2$ and $\cos(\tau)=\tan(\varphi)[1-\cos(\vartheta)]/\sin(\vartheta)$ according to Eq. (7) the 8×8 Hessian matrix of Table II contracts to the minimal 4×4 Hessian of Table I. This test justifies the assumption on the numerical precision with which the optimized coordinates and the second derivatives are obtained in these calculations.

TABLE I. Hessian matrix $(\hat{\mathbf{F}})$, optimized geometry, and elastic importance $(\Delta\mathcal{F})$ for polyethylene.

Variable	$\hat{\mathbf{F}}_{i,j}$				Optimum	$\Delta\mathcal{F}(\%)$
r_{CC}	1.12				1.513	83.0
r_{CH}	0.09	2.17			1.112	0.0
ϑ	0.19	−0.10	0.46		113.6°	46.4
φ	0.25	−0.17	0.61	3.07	109.4°	16.3
	r_{CC}	r_{CH}	ϑ	φ		

With the use of the eight configurational parameters, the artifactual effect of neglecting the CH bond's relaxation is avoided, as the CH bonds are now fixed with their bond angle(s) and a dihedral angle. The deformation of only the CC bonds does not induce big deformations in the CH groups, $F_{\vartheta\vartheta}=0.39$ becomes smaller and the coupling between CCC bond angle and CCH or CCCH angles decreases.

In Table II the $\dot{\mathbf{x}}$ column [calculated according to Eq. (A5)] shows what changes are expected in the equilibrium coordinates after elongations. The derivatives $\dot{r}_{\mathrm{CC}}$ and $\dot{\vartheta}$ cannot be compared directly, as the former is dimensionless whereas the latter is a quantity in radian/angstrom. A comparable property is (besides $\Delta\mathcal{F}$) how the total strain is distributed among the different degrees of freedom. This can be characterized by

$$\Delta c_i \doteq \frac{\partial c(\mathbf{x})}{\partial \mathbf{x}_i}\cdot\frac{d\mathbf{x}_i}{dc}=\mathbf{g}_i\dot{\mathbf{x}}_i \tag{15}$$

listed in column Δc.

With these coordinates the relaxation of the carbon-hydrogen bonds does not change the Young's modulus more than 3%; they could have been kept frozen during the calculation within the accuracy used. Neither these CH bond changes contribute to the cell length Δc showing that strain is not transferred to these degrees of freedom. These facts do not mean, that the bonds themselves do not change, $\dot{\tau}$ and $\dot{\varphi}$ are one-fourth and one-fifth of the change of the CCC bond angle $(\dot{\vartheta})$, respectively.

TABLE II. Hessian matrix, optimized coordinates, and their elastic response for polyethylene.

Variable	$\hat{\mathbf{F}}$								Optimum	$\Delta\mathcal{F}(\%)$	$\dot{\mathbf{x}}$	$\Delta c(\%)$
r_{CC}	1.11								1.513	84.0	0.69	57.6
r_{CH1}	0.05	1.07							1.112	0.0	0.00	0.0
r_{CH2}	0.05	0.02	1.07						1.112	0.0	0.00	0.0
ϑ	0.12	-0.03	-0.03	0.39					113.7°	45.7	1.03	42.4
φ_1	0.02	-0.00	-0.01	0.02	0.17				109.4°	0.9	-0.25	0.0
φ_2	0.02	-0.01	-0.00	0.02	0.03	0.17			109.4°	0.9	-0.25	0.0
τ_1	0.05	-0.00	-0.03	-0.07	0.01	0.05	0.17		122.5°	0.4	0.20	0.0
τ_2	0.05	-0.03	-0.00	-0.07	0.05	0.01	0.09	0.17	$-122.5°$	0.4	0.20	0.0
	r_{CC}	r_{CH1}	r_{CH2}	ϑ	φ_1	φ_2	τ_1	τ_2				

The longitudinal elastic constants calculated according to Eq. (6) from the two polyethylene Hessians are the same up to the four significant digits given in Table VII. The Young's modulus, $Y=323.2$ GPa is similar to most of the calculated values in the literature.[1,2,5–8] One expects the TZVP basis set and the density-functional method to predict a Young's modulus close to a HF+MP2 calculation in a multivalence polarized basis set. The 336 GPa value of Crist and Hereña[1] is in a reasonable agreement with our result. The 276 GPa of Suhai[4,3] is not justified by the present calculations. The possible reasons for that extreme low value has been discussed in Ref. 1, where the danger of the linear dependency of the basis set in crystal-orbital calculations was suspected to cause the discrepancy. The calculations presented in this paper use crystal orbitals built from extended basis sets but the Young's modulus does not approach Suhai's value.

The direct elongation-relaxation method using five different elongations resulted in $\mathcal{F}=1.069$ hartree/angstrom, in accordance with the Hessian based value.

2. Polytetrafluoroethylene (planar)

Although for teflon the optimal configuration under normal pressure differs slightly from the planar one, for comparison with polyethylene we optimized the structure by constraining the carbon backbone to be in a plane. The five parameters (r_{CF}, ϑ, r_{CF}, φ, and τ) induce the σ_h planar symmetry whereas the σ_v plane is not used explicitly but expected to be maintained by the optimization procedure itself. It was needed in order to decouple the CF bonds as much as possible from the CCC bond distortions, as was learned from the PE study. In Table III the results are given for PTFE. The Hessian for PE in the same parametrization is also indicated in parentheses. The replacement of hydrogens with fluorines slightly softens the chain, the CC bond stretching constant is smaller, and the bond itself becomes longer. The more pronounced difference appears in the force constants which describe the distortion of the CF bonds, $F_{\tau\tau}$ becomes approximately twice as big as that of PE, but these changes do not considerably affect the longitudinal elastic behavior. The total neglect of CF relaxation (r_{CF}, φ, and τ all frozen) gives an elastic modulus 3% higher, than the full calculation.

The five calculations with strained geometry result in $\mathcal{F}=1.013$ which is 2% higher than the value from the Hessian in Table VII. This is acceptable in the numerical precision expected.

3. Polytetrafluoroethylene (helix)

The common conformation of crystalline PTFE is a (13/6) helix, that is a helix with 163.5° screw angle.[18,19] The calculations show that the helix is not formed primarily because of the crystal structure; the single chain already favors this geometry. The softening of the chain is expected with respect to the planar configuration. Out of plane relaxations should decrease the Young's modulus and the rate of this is investigated here. In the calculations we kept the two CF bonds equivalent because of symmetry considerations. The length of the two bonds, their bond angles φ, and dihedral angles τ with the corresponding CC bonds and CCC planes are kept equal: $\measuredangle \mathrm{C}^{+}\mathrm{CF}^{1}=\measuredangle \mathrm{C}^{-}\mathrm{CF}^{2}$ and $\measuredangle \mathrm{C}^{-}\mathrm{C}^{+}\mathrm{CF}^{1}=\measuredangle \mathrm{C}^{+}\mathrm{C}^{-}\mathrm{CF}^{2}$ where $\mathrm{C}^{+}(\mathrm{C}^{-})$ is the next(previous) carbon neighbor to C. The dihedral angle (γ) between subsequent CCC sheets has been introduced as the sixth parameter. Global optimization (see Table IV) shows an absolute minimum

TABLE III. Hessian matrix ($\hat{\mathbf{F}}$), optimized geometry, and elastic importance ($\Delta\mathcal{F}$) for planar teflon (numbers in parentheses are values for polyethylene).

Variable	$\hat{\mathbf{F}}$					Optimum	$\Delta\mathcal{F}(\%)$
r_{CC}	0.99(1.11)					1.561	85.8
$r_{\mathrm{CF}}(r_{\mathrm{CH}})$	0.25(0.09)	3.38(2.19)				1.347	0.0
ϑ	0.13(0.12)	$-0.18(-0.05)$	0.39(0.39)			113.1°	39.6
φ	0.04(0.05)	$-0.09(-0.04)$	0.08(0.05)	0.65(0.41)		108.5°	2.7
τ	0.06(0.09)	$-0.16(-0.06)$	$-0.11(-0.13)$	0.40(0.12)	1.07(0.52)	120.4°	1.6
	r_{CC}	$r_{\mathrm{CF}}(r_{\mathrm{CH}})$	ϑ	φ	τ		

TABLE IV. Hessian matrix ($\hat{\mathbf{F}}$), optimized geometry, and strain contributions for helical PTFE.

Variable	$\hat{\mathbf{F}}$						Optimum	$\Delta\mathcal{F}(\%)$	$\Delta c(\%)$
r_{CC}	1.00						1.555	77.8	56.6
ϑ	0.13	0.41					112.3°	44.2	42.4
γ	0.01	0.01	0.11				161.3°	0.9	1.0
r_{CF}	0.27	−0.15	0.01	3.39			1.347	0.0	0.0
φ	0.07	0.09	0.03	−0.04	0.65		108.7°	5.2	0.0
τ	0.07	−0.17	−0.05	−0.16	0.337	1.27	120.5°	3.3	0.0
	r_{CC}	ϑ	γ	r_{CF}	φ	τ			

at $\gamma = 161.3°$, which corresponds to a helical rotational angle 164.5° in good agreement with experimental crystal data and calculated optimized structure of others.[23,24]

The possibility to relax the system out of plane does not change the elastic properties too much; the Young's modulus changes with some percentages, the trend of which (softening) is correct but the value is of the same order as the error in the calculations. The 161° dihedral angle turns out to be a small distortion from the planar 180° case. The small $F_{\gamma\gamma}$ force constant does not decrease the Young's modulus substantially as long as changes in γ have a small effect on the cell length. The indirect contribution to Y through the coupling to the most important coordinates r_{CC} and ϑ is small as well which is due to the small ~ 0.01 coupling constants. The fact, that slight deformations from the planar structure do not have a drastic effect on the elasticity is rather important. Even if the force constants related to the torsional degrees of freedom would be well described in the local density approximation, their small value would come out with a large relative error from the numerical total energy differences. Big changes in the elastic behavior are expected in more twisted configurations, like in the *gauche* one for which $\gamma \sim 57°$. Very careful determination of the torsional force constants then becomes inevitable.

It can be observed, that the relaxation of the CF bonds is now twice as important as it is for the planar configuration. The total neglect of changes in r_{CF}, φ, and τ would result in a chain which is 6.3% harder. In addition keeping γ frozen at its equilibrium value would result in a 6.5% change instead, which shows that this effect does not originate from the coupling to the CCC dihedral angle.

B. Polyamides

1. Polyglycine

Polyglycine, as the simplest polypeptide has been of interest because of its biological importance. The secondary structure of those proteins mostly does not possess periodicity in nature. Among the folded-twisted chains, the most important periodic structures are grouped in the β-sheet (PG-I) and the α-helix (PG-II) families. The α-helix type configurations are better studied in a biological context[25] while the nearly planar configurations are more relevant to a solid state approach. Below we report in our calculations on a prototype for a polyglycine-I chain, where the unit cell consists of a [-C$^{\alpha}$H$_2$-CONH-] group which is then used to build a β-sheet strictly planar zigzag chain. In real crystals[26] the two torsional angles, Φ around the NC$^{\alpha}$ and Ψ around C$^{\alpha}$C can have a variety of values different from 180°. Distortions from perfect planarity give rise, e.g., to rippled sheets, pleated sheets, or helical configurations. The interchain hydrogen bonds may prefer one of these forms if the chains are in a crystal, but for a single chain there is no such favored configuration. With the modest 321G (Ref. 27) basis set our optimization attempts could not find a stable minimum out of the plane. Dasgupta *et al.*[9] parametrized their force field for the nearly planar α forms of nylons in which case they found $\Phi = \Psi$ between 163° and 168°, but their torsional potential for noncrystalline test molecules is so flat on going to 180° that it is not convincing to consider the nonplanar structure for a chain. The polyglycine II family is characterized by the *gauche* α-helix configuration. The elastic properties of such a single helix must be dominated by the soft torsions at the methyl CH$_2$ group which requires very accurate force constants for this mainly van der Waals interaction. The investigation of this structure is out of the focus of this paper, especially as the elastic properties of such chains are more determined by their interaction with their environment than by their isolated structure.

The planar structure can be fixed by 13 parameters when the two CH bonds are kept symmetric. The optimized structure is given in the Table V with some representative elements of the Hessian. This skeleton Hessian contains those second derivatives, which have an absolute value greater than 0.10. The longitudinal force constant is obtained from the complete Hessian, not from the skeleton since small values from the Hessian cannot be omitted if they contribute to or even dominate the linear elastic response.

The dominant response to stress is at the CC$^{\alpha}$N bond angle; other angles in the zigzag backbone bend much less. This is rather unexpected in view of the fact that the C$^{\alpha}$NC angle has a lower force constant but hardly absorbs strain. A similar effect can be mentioned in the bond stretching contributions. The NC bond is the hardest of all in the backbone but it gives the largest response. The importance of these unexpected deformations is due to the constraint to keep the chain linear. If more methyl groups appear between the amides the distortion of the latter is not required so much since the softer methyl groups can absorb the strain. The exclusion of all degrees of freedom not directly associated with the backbone chain, i.e., freezing all the variables: 3, 4, 5, 8, 9, 10, 13 (as they are numbered in Table V) would give a Young's modulus which is 8.9% higher. This error reduces to 4.1% if the OCC$^{\alpha}$ bond angle is allowed to relax.

TABLE V. Skeleton Hessian($\hat{\mathbf{F}}_{i,j}$), optimized coordinates, and elastic contributions for planar polyglycine.

Variable name	index	$\hat{\mathbf{F}}_{i,j}$				Optimum	$\Delta\mathcal{F}(\%)$	$\Delta c(\%)$
r_{NC}	1	$1.80_{1,1}$				1.335	20.8	19.7
$r_{\mathrm{CC}^{\alpha}}$	2	$1.04_{2,2}$				1.512	9.0	15.5
r_{OC}	3	$2.56_{3,3}$	$0.29_{3,1}$	$0.17_{3,2}$		1.239	0.5	0.0
r_{NH}	4	$1.37_{4,4}$				1.038	0.7	0.0
r_{CH}	5	$2.24_{5,5}$				1.110	0.0	0.0
$r_{\mathrm{C}^{\alpha}\mathrm{N}}$	6	$1.35_{6,6}$				1.428	12.8	16.7
$\vartheta_{\mathrm{NCC}^{\alpha}}$	7	$0.48_{7,7}$	$0.10_{7,2}$	$-0.16_{7,3}$		116.5°	6.8	10.3
$\vartheta_{\mathrm{OCC}^{\alpha}}$	8	$0.54_{8,8}$	$-0.15_{8,1}$	$0.15_{8,2}$	$0.25_{8,7}$	120.4°	3.2	0.0
φ_{HNC}	9	$0.22_{9,9}$	$-0.11_{9,4}$			125.8°	1.9	0.0
$\varphi_{\mathrm{HC}^{\alpha}\mathrm{C}}$	10	$0.42_{10,10}$				110.7°	0.9	0.0
$\vartheta_{\mathrm{CC}^{\alpha}\mathrm{N}}$	11	$0.46_{11,11}$	$0.20_{11,2}$			106.0°	34.6	35.4
$\vartheta_{\mathrm{C}^{\alpha}\mathrm{NC}}$	12	$0.30_{12,12}$	$0.10_{12,1}$	$-0.12_{12,4}$	$0.13_{12,9}$	122.1°	0.7	2.3
$\tau_{\mathrm{HC}^{\alpha}\mathrm{CN}}$	13	$0.53_{13,13}$	$-0.16_{13,6}$	$0.14_{13,11}$		58.85°	1.1	0.0

The role of this bond angle is worth commenting upon. The oxygen is not in the main backbone, so it does not affect the length directly. *In this parametrization*, however, it contributes to the Young's modulus to a remarkable extent through its coupling to other coordinates. Applying stress to the chain, the NCC$^{\alpha}$ angle changes which forces the rotation of the OC bond as it is fixed in the plane with respect to the CC$^{\alpha}$ bond through the OCC$^{\alpha}$ bond angle. The induced change in the bond angle OCN is not favored so that the oxygen must relax. Let us introduce a new parametrization of the geometry by replacing $\vartheta_{\mathrm{OCC}^{\alpha}}$ with its other bond angle

$$\vartheta_{\mathrm{OCN}}=360°-\vartheta_{\mathrm{OCC}^{\alpha}}-\vartheta_{\mathrm{NCC}^{\alpha}} \tag{16}$$

and transform the Hessian according to Eq. (7) to the new coordinates. The diagonal force constant of $\vartheta_{\mathrm{NCC}^{\alpha}}$ will change from 0.48 to 0.51 and the weight of the new ϑ_{OCN} angle drops to 0.8% instead of the previous 3.2% for the $\vartheta_{\mathrm{OCC}^{\alpha}}$ angle. Using these coordinates the six parameters that fix the backbone give a longitudinal elastic constant only 5.4% higher than the full relaxation.

Calculations at five strained configurations give a longitudinal force constant $f=0.440$ with a fitting error of ± 0.002. This is in full agreement with the data calculated from the Hessian.

2. Nylon-3

The first element of the odd nylon series contains two methyl groups in the helical unit cell [-C$^{\alpha 2}$H$_2$-C$^{\alpha 1}$H$_2$-CONH-] which in this case is the translational cell as well. The planar zigzag configuration[18] is selected for the calculations, although all the remarks made for polyglycine about nonplanarity apply for the nylons. The two hydrogens of each methyl group are kept symmetric but the two pairs at the two groups are allowed to be different. The strict linearity of the main chain is assumed, which makes it necessary to exclude one coordinate from the backbone as the translational symmetry fixes the value of it with all the others given. This way 17 degrees of freedom are used in the structural optimization and the ''push and pull'' calculations. The Hessian is obtained with keeping four bond length parameters frozen. These bonds are out of the backbone chain and assumed not to contribute to the longitudinal elasticity. The optimized values, diagonal elements of the Hessian, and longitudinal elastic data of the coordinates are listed in Table VI. Some qualitative remarks can be made for comparison with polyglycine. The NC and C$^{\alpha}$N bonds become longer, these longer bonds are also considerably softer, but the deformations are tending to appear more at the methyl groups than at the rigid amide planes. The forced deformation of the NC bond, which takes one fifth of the strain in glycine is now not required; instead of this the two CCC bond angles centered at the two α carbons deform upon elongations since these angles are the softest part of the chain. The Hessian looks strange at first sight, as the second derivatives seem to differ considerably from the corresponding ones for either

TABLE VI. Elastic data and optimized coordinates for nylon-3.

Variable	$\hat{\mathbf{F}}_{i,i}$	Optimum	$\Delta\mathcal{F}(\%)$	$\dot{\mathbf{x}}$
r_{NC}	1.62	1.356	8.5	0.13
$r_{\mathrm{CC}^{\alpha 1}}$	0.98	1.514	12.4	0.20
$r_{\mathrm{C}^{\alpha 1}\mathrm{C}^{\alpha 2}}$	1.09	1.507	10.7	0.17
r_{OC}		1.230		
r_{NH}		1.021		
$r_{\mathrm{C}^{\alpha 1}\mathrm{H}}$		1.109		
$r_{\mathrm{C}^{\alpha 2}\mathrm{H}}$		1.107		
$r_{\mathrm{C}^{\alpha 2}\mathrm{N}}$	1.23	1.446	12.4	0.18
$\vartheta_{\mathrm{NCC}^{\alpha 1}}$	0.86	116.9°	7.0	0.22
$\vartheta_{\mathrm{CC}^{\alpha 1}\mathrm{C}^{\alpha 2}}$	0.65	109.0°	14.3	0.31
ϑ_{OCN}	0.54	122.0°	3.1	-0.16
φ_{HNC}	0.21	121.0°	0.6	-0.10
$\varphi_{\mathrm{HC}^{\alpha 1}\mathrm{C}}$	0.42	109.5°	0.8	-0.08
$\varphi_{\mathrm{HC}^{\alpha 2}\mathrm{C}^{\alpha 1}}$	0.47	110.6°	0.8	-0.08
$\vartheta_{\mathrm{C}^{\alpha 1}\mathrm{C}^{\alpha 2}\mathrm{N}}$	0.73	111.2°	13.1	0.32
$\tau_{\mathrm{HC}^{\alpha 1}\mathrm{CN}}$	0.49	58.72°	0.9	-0.08
$\tau_{\mathrm{HC}^{\alpha 2}\mathrm{C}^{\alpha 1}\mathrm{C}}$	0.54	57.76°	0.3	-0.05

TABLE VII. Longitudinal force constants and Young's moduli.

	Screw angle	c[Å]	$\mathcal{F}$[H/Å^2]	f[H/Å]	Area [Å^2]	Y[GPa]
Polyethylene	180.0°	1.266	1.068	1.352	18.24[a]	323.2
Polytetrafluoroethylene	180.0°	1.302	0.991	1.291	24.84[a]	226.5
Polytetrafluoroethylene	164.5°	1.286	0.977	1.256	24.84[a]	220.5
Polyglycine	180.0°	3.566	0.435	1.553	17.52[b]	386.4
Nylon-3	0.0°	4.872	0.308	1.501	17.52[a]	373.6

[a] Crystal Ref. 18.

[b] Taken to be equal to nylon-3.

the vinyl polymers or polyglycine. For example, the diagonal elements of the angle bendings at the alpha carbons are nearly twice as big as for PE or PTFE (Table III). This is neither a computational error nor a physical hardening of these groups, but comes from the translational constraint. There is an extra chemical degree of freedom not explicitly appearing in the calculation namely the bond angle C$^{\alpha 2}$NC which becomes a dependent variable if one keeps all the NC bonds in the chain parallel. Any time a deformation is done in the remaining degrees of freedom this bond angle is implicitly forced to change in order to fulfill the matching condition between the cells, to preserve the pure translational symmetry. This way the force constant of the C$^{\alpha 2}$NC angle shows up implicitly in all the elements of the Hessian. The quantitative way, how it is counted in the present Hessian, is a question of geometry. As a qualitative example, a look at the geometry gives a rough guess, that a change in the CCC angles at the alpha carbons induces an approximately equal change of the constrained angle. The diagonal Hessian elements of the angles at the alpha carbons are the sum of CCC and CNC force constants. The estimated value for the CCC angle is about 0.4, while for CNC it is 0.3 (e.g., from Table V on polyglycine) which sums up to the value of 0.7 similar to what is found in Table VI.

The calculated elastic modulus is again given in Table VII. The 7-in-backbone variables are responsible for most of the elasticity, they alone give $f=1.597$ which is 6.4% higher than the full one. From $\dot{\mathbf{x}}$ of Table VI one can see, that the largest changes occur at the alpha carbons. The five-point elongation-relaxation calculations relaxing all 17 degrees of freedom are fitted and give $\mathcal{F}=0.308\pm 0.006$, which is in full accordance with the value calculated from the reduced Hessian with 13 degrees of freedom. The inclusion of an additional methyl group results in a 3.3% softening with respect to polyglycine.

IV. CONCLUSION

The calculation of the Young's modulus for single helical chains has been carried out. It has been shown that some degrees of freedom of the polymer can be omitted from such a theoretical calculation without a considerable loss of precision. This simplification however can be done only if the side groups which are expected not to affect the main chain's elastic response very much, are defined by carefully chosen appropriate coordinates.

The direct elongation-relaxation procedures are shown to give the same elastic constants as the Hessian based method. Although the latter reveals a more detailed picture about what is happening in the polymer under stress, the former becomes incomparably more economical if the degrees of freedom are large. The evaluation of the Hessian scales quadratically with this number, whereas for a small strain some fixed number (3–5) of relaxation steps is required to reach a reasonable convergence.

APPENDIX: LONGITUDINAL ELASTICITY FROM THE HESSIAN

The constrained minimization (1) implicitly defines $\mathbf{x}(c)$. Starting from the Lagrangian equation

$$\mathbf{G}=\lambda\mathbf{g}, \tag{A1}$$

where $\mathbf{G}=\partial E/\partial\mathbf{x}$ and $\mathbf{g}=\partial c/\partial\mathbf{x}$ an explicit expression for

$$\dot{\mathbf{x}}\big|_0 \doteq \frac{d\mathbf{x}(c)}{dc}\bigg|_0 \tag{A2}$$

can be derived (an overdot is used to denote differentiation with respect to c). Indeed, multiplying Eq. (A1) with $\dot{\mathbf{x}}$ and rewriting the constraint as $(\dot{\mathbf{x}},\mathbf{g})=1$ one gets $\lambda=(\dot{\mathbf{x}},\mathbf{G})$ and the Lagrange equation becomes

$$\mathbf{G}=(\dot{\mathbf{x}},\mathbf{G})\mathbf{g}. \tag{A3}$$

The derivative of this equation with respect to c and taken *at equilibrium* (where $\mathbf{G}=0$ and $\dot{\mathbf{G}}=\hat{\mathbf{F}}\dot{\mathbf{x}}$) is $\hat{\mathbf{F}}\dot{\mathbf{x}}=(\dot{\mathbf{x}},\hat{\mathbf{F}}\dot{\mathbf{x}})\mathbf{g}$. With an invertible Hessian this can be written as

$$\dot{\mathbf{x}}=(\dot{\mathbf{x}},\hat{\mathbf{F}}\dot{\mathbf{x}})\hat{\mathbf{F}}^{-1}\mathbf{g} \tag{A4}$$

which when multiplied with $\mathbf{g}$ gives

$$1=(\dot{\mathbf{x}},\hat{\mathbf{F}}\dot{\mathbf{x}})(\mathbf{g},\hat{\mathbf{F}}^{-1}\mathbf{g}) \quad\text{and}\quad \dot{\mathbf{x}}=\frac{\hat{\mathbf{F}}^{-1}\mathbf{g}}{(\mathbf{g},\hat{\mathbf{F}}^{-1}\mathbf{g})}. \tag{A5}$$

Combining this result with definitions (1) and (2) one has

$$\mathcal{F}=\frac{d^2}{dc^2}E(c)\bigg|_0=(\dot{\mathbf{x}},\hat{\mathbf{F}}\dot{\mathbf{x}})=(\mathbf{g},\hat{\mathbf{F}}^{-1}\mathbf{g})^{-1}.$$

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